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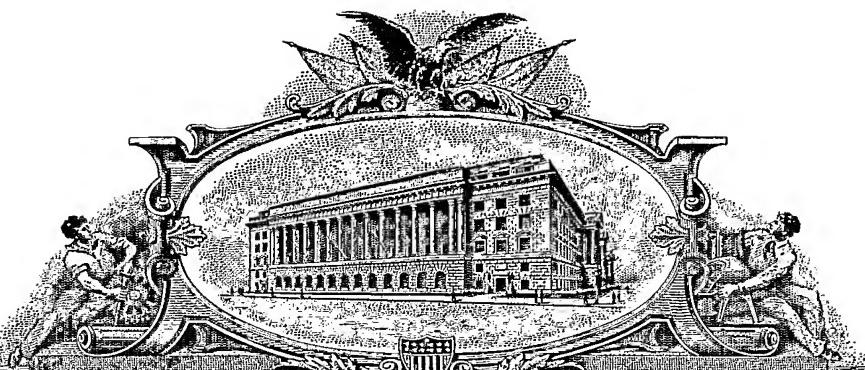
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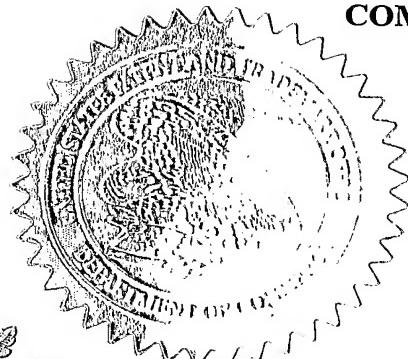
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William G.		SKENE		Montreal, QC, Canada																															
<b>TITLE OF THE INVENTION (500 characters max)</b>																																			
SYNTHESIS OF NOVEL CONDUCTING AND CONJUGATED THIOPHENES BASED ON OLIGO AND POLYZOMETHINES FOR CONDUCTING MATERIALS																																			
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Respectfully submitted,

[Page 1 of 2]

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## **SYNTHESIS OF NOVEL CONDUCTING AND CONJUGATED THIOPHENES BASED ON OLIGO AND POLYAZOMETHINES FOR CONDUCTING MATERIALS**

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**Abstract:** Conjugated oligomers and polymers consisting of aromatic thiophene cores involving easy condensation are presented. The conjugated materials are obtained by simple and efficient condensation of an aryl diamine and an aryl dialdehyde or a difunctional aryl moiety comprising both an aldehyde and an amine. Condensation of the complementary moieties at temperatures ranging from ambient to refluxing temperatures in various solvents, lead to conjugated oligomers and polymers that can subsequently be cast into thin films. Oligomerization and polymerization

can be done under mild conditions with removal of the resulting water bi-product responsible for shifting the equilibrium in favour of the conjugated products. The resulting conjugated compounds can be made conducting with dopants affording electrically conducting materials of either p-type or n-type conductors depending on the dopant selected.

#### **Field of Invention:**

The invention relates to the synthesis of thiophene based oligo- and polyazomethines and their subsequent doping for the use of solutions of such complexes for the preparation for conducting materials and devices.

#### **Background of the Invention:**

Conjugated polymers have received much attention because of the many new possibilities for devices combining unique optical, electrical, and mechanical properties that exist.<sup>1</sup> A few such applications of conjugated polymers involve organic light emitting diodes (OLEDs) and molecular wires to be used in flexible light displays and/or low power consumption products.<sup>2,3</sup> Because of the many interesting properties they posses, these materials have been heavily investigated both in terms of their synthesis and for their various electrical optical properties and have received widespread recognition industrially and academically recognized via a recent Nobel prize. Synthesis of these industrially relevant materials has evolved from elimination reactions to more elegant coupling strategies. However as attractive as these polymers are for their physical properties, the main synthetic methods pursued are not straightforward<sup>4-6</sup> and require Suzuki,<sup>7</sup> Wittig,<sup>8</sup> or Mitsunobu<sup>9</sup> synthetic strategies, or electropolymerization.<sup>10</sup> Such methods subsequently entail challenging and tedious purifications to isolate the desired polymers and removal of the metal bi-products and are often compounded with low to moderate yields only

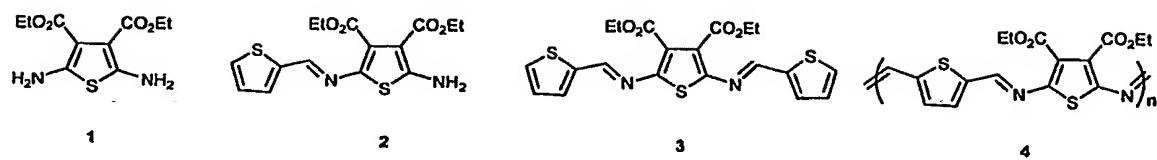
applicable on small scale.<sup>4,5</sup> Even though conjugated aromatic polyazomethine compounds have been known for many years, and their properties and methods of preparation have been discussed in a review article,<sup>11</sup> we represent the first such compounds involving thiophene units. The advantage of such condensation strategy is the ease of purification with the reaction being amenable to a plethora of reagents. Moreover, it does not necessitate the use of anhydrous solvents and strict oxygen free reaction environments, unlike conventional conjugation methods. We report the first facile synthetic route for conjugated thiophenes not requiring difficult reaction conditions and their subsequent characterization. The driving force of this simple oligomerization is the thermodynamically desirable conjugation formation leading to a new class stable thiophene containing materials exhibiting interesting photophysical and conducting properties.

#### **Detailed Description of the Invention:**

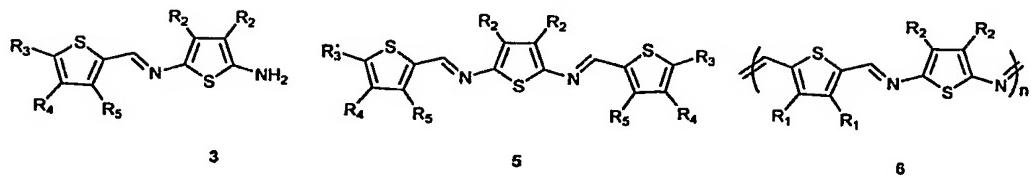
The invention relates to the synthesis of conjugated aromatic oligo and polyazomethines that are prepared by reacting one or more aromatic diamines with one or more aromatic dialdehydes either in solution or in a molten state, using procedures described herein. Of these aromatic units, one is a thiophene core affording the polyazomethine **10** or **11** illustrated in Scheme 4. Preferably, the polymeric compounds are prepared by the reaction of one dialdehyde with an equimolar amount of one diamine, or of one diamine with an equimolar amount of one dialdehyde with one or both aryl components being a thiophene. The integer Y from scheme 4 may a 6 member homocyclic ring, 6 member heterocyclic ring comprising one to three nitrogen atoms, a 5 member heterocyclic ring comprising a sulfur, nitrogen, tellurium, or selenium atom. Preferably the integers R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, and R<sub>5</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-

$C_4$  aliphatic chains with  $C_1-C_{12}$  alkoxy groups,  $C_6-C_{14}$  aromatic systems, ester groups  $CO_2Z$  with  $Z$  aliphatic  $C_2-C_{12}$ , aliphatic  $C_2-C_4$  aliphatic chains or cyano. The process also related to a conjugated conducting polymer of the general structure of **8** (Scheme 3) obtained by the condensation of difunctional monomer containing an aryl monoamine and monoaldehyde (**7**) with the integers  $R_1$  and  $R_2$  may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. The said description may also include multifunctional aryl moieties comprising of more than two aldehydes or amine moieties. The integers  $R_3$  may be also be aliphatic  $C_2-C_{12}$ , aliphatic  $C_2-C_4$  aliphatic chains with  $C_1-C_{12}$  alkoxy groups,  $C_6-C_{14}$  aromatic systems, ester groups  $CO_2Z$  with  $Z$  aliphatic  $C_2-C_{12}$ , aliphatic  $C_2-C_4$  aliphatic chains or cyano, nitro, halogens, carboxylic acids, amines, carboxaldehydes, identical or different. The resulting materials can be spin coated into thin films of varying thickness from casting of solutions such as but not limited to THF, chloroform, dichloromethane, alcohols, DMF, etc. The conjugated materials can be made conducting by doping with p-type dopants such as for example but not limited to iodine. The conjugated materials can be made conducting by doping with n-type dopants such as for example but not limited to sodium naphthalide,  $SbF_5$ ,  $AsF_5$ ,  $PF_5$ ,  $AgX$ ,  $NO_2X$ , and  $NOX$  where  $X$  is an unreactive, non-nucleophilic anion. The molecular weight of the resulting polymers can be controlled by variation in the reaction concentrations.

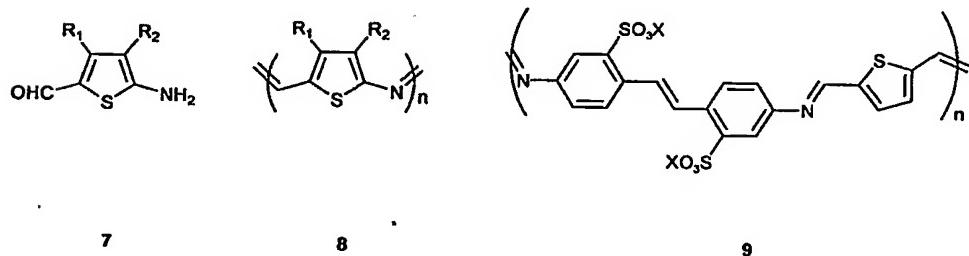
Following are examples of preferred conjugated aromatic oligo and polyazomethines that can be used in the preparation of compositions of the present invention:



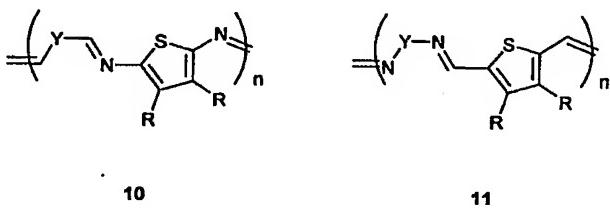
**Scheme 1**



**Scheme 2**



**Scheme 3**



**Scheme 4**

### General method of oligoazomethine synthesis.

Selective oligomerization leading to dimer such as 2 can be done at temperatures ranging from 25° to 120° C under normally atmosphere or inert atmosphere such as nitrogen or argon with

alcohol solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc. The use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization. Dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product. Generally one stoichiometric equivalent of aldehyde is added to one stoichiometric equivalent of diamine and allowed to react between 0.5 to 36 hours till judged complete by TLC analyses. The solvent is subsequently removed under vacuum and the desired product obtained by as is or further purification, if required, can be in the form of flash chromatography over silica gel or activated neutral aluminum oxide.

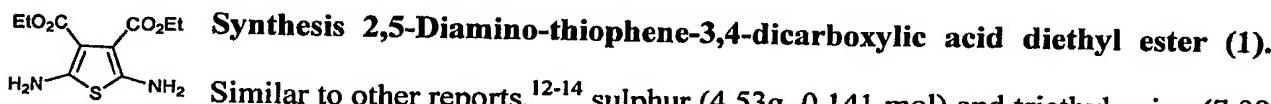
Selective oligomerization leading to trimer such as a symmetric **3** can be done according to procedure outlined for **2** through the use of two stoichiometric equivalents of aldehyde with one stoichiometric equivalent of diamine. Asymmetric trimers analogues of **3** can be obtained by reaction conditions outlined for **2** using one stoichiometric equivalent of aldehyde added one stoichiometric equivalent of diamine followed by the additional one stoichiometric equivalent of aldehyde added to the reaction mixture upon complete dimer formation.

#### **General method of polyazomethine synthesis**

For activated monomers, typically 80 to 100 mg of the diamine monomer were charged into a 100 ml round bottom flask then dissolved in between 60 and 75 ml of the polymerization solvent to

which is then added an exact stoichiometric amount of dialdehyde monomer. Suitable polymerization solvents are absolute ethanol, chloroform, methanol, anhydrous toluene, DMSO (methyl sulfoxide), DMF (N,N-dimethyl formamide), NMP (N-methyl pyrrolidinone), water, but may also include others. For the polymers examined, DMSO promoted the fastest polymerization rates. A catalyst is not required for some monomers, but in general, the apparent rates of reaction are greatly accelerated with its use. One can add 10% molar of, typically trifluoroacetic acid or acetic acid, but may also include mineral and other organic acids. The polymerization reaction may also proceed in the absence of solvent. The reaction mixture is then heated between 50° – 130° C for a period between 0.5 to 16 hours. In the case of low boiling point solvents, the polymer is isolated by removing the solvent under reduced pressure and then dried under vacuum. For less volatile solvents, the polymers are subsequently used without isolation. For the polymerization in water, the reaction was typically done at room temperature under moderately alkaline conditions. An emulsion catalyst such as benzyltriethyl ammonium chloride, may also be used for imine polymerization involving hydrophobic and hydrophilic monomers.

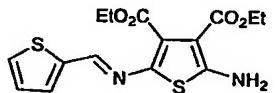
#### EXAMPLE 1, Scheme 1



Similar to other reports,<sup>12-14</sup> sulphur (4.53g, 0.141 mol) and triethylamine (7.09 mL, 0.0509 mol) were stirred at room temperature in DMF (15 mL) in a 250 mL three necked flask whereupon the solution turned red in colour after 30 minutes. Ethylcyanoacetate (20.4 mL, 0.192 mol) diluted in DMF (5 mL) was subsequently added dropwise over 30 minutes resulting in the deepening of the colour. The opaque solution was allowed to stir under ambient condition for

three days after which the solvent was pumped off under vacuum leaving a brown solid. The solid was loaded onto a silica gel column and eluted with hexane gradient up to 35 % ethyl acetate. The procedure was repeated a second time to obtain the 2.15 g (22 % yield) of title compound as gold flaky crystals. M.p. 155° – 158° C.  $^1\text{H}$  NMR (300MHz, [D] DMSO):  $\delta$  = 4.06 (q, 4H,  $J$ = 7.1), 1.17 (t, 6H,  $J$ =7.1).  $^{13}\text{C}$  (300MHz, [D] chloroform):  $\delta$  = 165.6, 148.9, 104.5, 60.4, 14.8. EI-MS: m/z 258.1 ([M] $^+$ , 80%), 212 ([M-C<sub>2</sub>H<sub>5</sub>O] $^+$ , 100%). Anal. calc. For C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>S (258.30): C 46.50, H 5.46, N 10.85, O 24.78, S 12.41 found: C 45.89, H 5.10, N 10.47, S 12.01.  $\lambda_{\text{max}}$  (acetonitrile) = 304 nm,  $\lambda_{\text{fl}}$  (acetonitrile) = 566 nm.

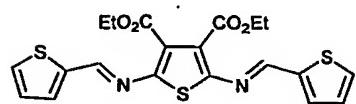
## EXAMPLE 2, Schema 1



**Synthesis of 2-Amino-5-[(thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester.** In a 250 mL flask, 50 ml absolute ethanol was dissolved 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (470 mg, 5.0 mmol) followed by 2-thiophene carboxaldehyde (646 mg, 2.5 mmol). After the addition of one drop of acetic acid, the solution was stirred at room temperature for 4 days. The solvent was then removed from the resulting orange solution and the residue was purified by flash chromatography (SiO<sub>2</sub>) using 20 % ethyl acetate / hexane to afford the title compound as a yellow solid (454 mg, 52 %). M.p. = 145° - 147° C.  $^1\text{H}$  NMR (200 MHz, [D] chloroform):  $\delta$  = 9.94 (s, 1 H), 8.06 (s, 1 H), 7.20 (t, 1 H), 7.18 (d, 1 H), 7.12 (m, 1 H), 7.02 (m, 1 H), 4.41 (t, 2 H), 4.24 (q, 2 H), 1.48 (t, 3 H), 1.29 (t, 3 H).  $^{13}\text{C}$  NMR (50 MHz, [D] chloroform):  $\delta$  = 164.5, 159.9, 145.9, 142.7, 134.0, 131.2, 130.2, 127.9, 102.9, 61.6, 60.3, 14.5, 14.3. FAB-MS: m/z 351.8 ([M] $^+$ , 100%). Anal. calc. for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (352.06): C 51.12, H 4.58, N 7.95, O 18.16, S 18.20 found: C 51.21, H 4.63, N

7.77, S 17.81.  $\lambda_{\text{max}}$  (DMSO) = 402 nm.  $\epsilon$  (DMSO) =  $3.6 \times 10^4 \text{ M}^{-1} \text{ dm}^{-1}$ ;  $\lambda_{\text{max}}$  (acetonitrile) = 408 nm,  $\lambda_{\text{fl}}$ (acetonitrile) = 604 nm.

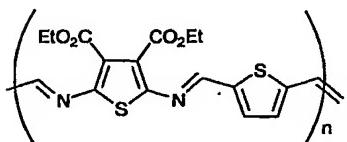
### EXAMPLE 3, scheme 1



**2,5-Bis-[(thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (2).**

17.7  $\mu\text{L}$  of 2-thiophene carboxaldehyde (21.7 mg, 0.1935 mmol), and 0.995  $\mu\text{L}$  of trifluoroacetic acid (1.487 mg, 0.0129 mmol, 16.7 mol%) were added to 10 mL of anhydrous ethanol. 20 mg of 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (0.0774 mmol) were dissolved into the solution, and the resulting mixture was allowed to stir under reflux for 2 days. The solvent was removed by rotary evaporation, and the remaining solid was washed with several portions of n-hexane, then recrystallized from acetone to yield fine red needle-like crystals (19.0mg, 55%). FAB-MS: m/z 447.1 ([M+], 70%).  $\lambda_{\text{max}}$  (acetonitrile) = 418 nm,  $\epsilon$ (acetonitrile) =  $2.3 \times 10^5 \text{ M}^{-1} \text{ dm}^{-1}$ ,  $\lambda_{\text{fl}}$ (acetonitrile) = 564 nm.

### EXAMPLE 4, scheme 2



**Synthesis of thiophene polyazomethine.** Commercially available 2,5-thiophenedicarboxaldehyde (6.5 mg, 0.046 mmol) were added to a 5 ml round bottom flask followed by 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (11.9 mg, 0.041 mmol) and 5 – 10 mol % of trifluoroacetic acid. The mixture was subsequently heated under nitrogen atmosphere for 12 hours without solvent. The resulting oil was used through the next step without further purification and was cooled, and the low molecular weight oligomers removed by washing with ethanol. The resulting purple

polymer is soluble in DMSO, DMF, and NMP to name but a few. DP = 3 601, M<sub>n</sub> = 87 541 g/mol.  $\lambda_{\text{max}}$  (DMSO) = 497 and 542 nm. Anal. calc. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> x 35.85 H<sub>2</sub>O: C 37.85, H 8.67, N 10.50, S 5.79 found: C 34.94, H 8.67, N 10.89, S 4.66.

Alternatively, 2,5-thiophenedicarboxaldehyde (4 mg, 0.029 mmol) were added to a 25 ml round bottom flask followed by 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (7.9 mg, 0.029 mmol) and 5 – 10 mol % of trifluoroacetic acid. The mixture was subsequently refluxed under nitrogen atmosphere for 12 hours with absolute ethanol and the polymer isolated upon removal of the solvent by evaporation and was used trough the next step without further purification. The resulting purple polymer is soluble in DMSO, DMF, and NMP to name but a few. DP = 74, M<sub>n</sub> = 26 686 g/mol.  $\lambda_{\text{max}}$  (DMSO) = 478 nm

Alternatively, in 7 ml anhydrous toluene was added 2,5-diamino-3,4-ethyl ester thiophene (146 g, 0.56 mmol) followed by 1,4-diaza-bicyclo[2.2.2]octane (DABCO; 411 mg, 3.66 mmol) added under argon followed by titanium (IV) chloride (100  $\mu$ l, 0.91 mmol). The temperature was raised and thiophene-2,5-dicarboxaldehyde (79 g, 0.56 mmol) dissolved in 10 ml anhydrous toluene was added. This mixture was refluxed under argon for 24 hours. The red wine coloured mixture obtained was cooled to room temperature and the precipitate was isolated by vacuum filtration. The polymer was isolated as deep blood red flakes readily soluble in alcoholic solvents, DMSO, DMF, and marginally soluble in chloroform.

For less reactive monomers, the polymerization was undertaken as follows. Typically, in a 50 mL flask, 150 mg of diamine monomer was dissolved in 10 ml of anhydrous and then 1,4-Diaza-bicyclo[2.2.2]octane (DABCO; 411 mg, 3.66 mmol) was added under nitrogen atmosphere. To

this solution was added 1.5 stoichiometric equivalents of titanium (IV) chloride (100 ml, 0.91 mmol) then the reaction mixture was heated to refluxed after the addition of one stoichiometric equivalent of monomer dialdehyde for a period of 24 hours. The polymer precipitated from solution and was isolated by filtration then washed with toluene and chloroform.

#### EXAMPLE 5, scheme 3



**Synthesis of poly(4,4'-diiminostilbene-2,2'-disulfonic acid thiophene).** A volume of 60 ml distilled water and a few drops of 2M sodium hydroxide was required to dissolve the commercially available 4,4'-diaminostilbene-2,2'-disulfonic acid (155 mg, 0.41 mmol). After the addition of 40 ml THF, was added 2,5-thiophenè dicarboxaldehyde (58 mg, 0.42 mmol) along with a catalytic amount of benzyltriethyl ammonium chloride. The red coloured solution was stirred at room temperature for two days then the solvent removed under reduced pressure to afford the polymer as a red solid that was recrystallized from ethanol.  $\lambda_{\text{max}}$  (water): 305 and 338 nm.  $M_w = 148\,094$ , PDI = 2.3, DP = 286.  $^1\text{H}$  NMR (200 MHz, [D] DMSO):  $\delta = 8.92$  (br, s, 2 H), 8.21 (br, s, 2 H), 7.80 (br, s, 6 H), 7.39 (br, s, 2 H). Anal. cald.  $C_{20}\text{H}_{12}\text{O}_6\text{N}_2\text{S}_3\text{Na}_2 \cdot 7.2\text{ H}_2\text{O}$ : C 37.06, H 4.11, N 4.32, S 14.84 found C 37.27, H 3.90, N 4.28, S 14.62. The  $^1\text{S}_{0,0} - ^0\text{S}_{0,0}$  (HOMO-LUMO) transition was calculated to be 65 kcal/mol (2.83 eV). From the absorption onset in the red region of the spectrum, a value can be calculated for the band gap of 51.3 kcal/mol (2.23 eV) for 1

#### EXAMPLE 6, preparation of pellets

Pellets for electrical conductivity testing were prepared by adding a measured amount of the polymer powder to a Beckman IR pellet press. The pellets were 1.3 cm in diameter with a thickness determined by the amount of material pressed and the pressure used.

Reliable conductivity data was obtained by drying the material thoroughly in vacuum at 25° to 100° C at 0.2 mm Hg for several hours after preparation of the pellets. The anhydrous pellets normally were removed and stored under nitrogen until testing.

#### **EXAMPLE 7, preparation of p-type doped pellets**

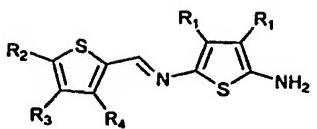
Iodine doping was done through the addition of iodine crystal to a chamber containing a pellet of polymer. The chamber then was evacuated causing immediate sublimation of iodine. Gaseous iodine remained in contact with a pellet for a period from about 1.5 to about 17 hours, whereupon the doped pellet was removed and stored under nitrogen until being tested.

#### **EXAMPLE 8, preparation of n-dopes pellets**

Doping of a polymer with sodium naphthalide may be accomplished by contacting the polymer powder with a slurry of sodium naphthalide in dry tetrahydrofuran. After the mixture is stirred under nitrogen for 24 hours, excess sodium naphthalide and solvent may be removed. The remaining solvent may be evaporated in a stream of nitrogen and the doped polymer may be dried as described above but at room temperature.

#### **What is claimed is:**

1. An electrically conducting oligomer with the composition comprising the material with the structure,



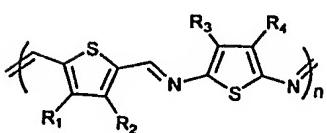
where the integers R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub>, or hydrogens. Substituents R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> may also be NO<sub>2</sub>. They may be identical or different permutations of the above radicals.

2. An electrically conducting oligomer with the composition comprising the material with the structure,



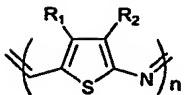
where the integers R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> or hydrogens. Substituents R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> may also be nitro. They may be identical or different permutations of the above radicals.

3. An electrically conducting oligomer with the composition comprising the material with the structure,



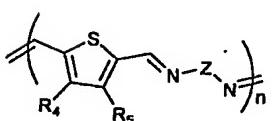
where the integers R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> or hydrogens. Substituents R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> may also be nitro. They may be identical or different permutations of the above substituents.

4. An electrically conducting oligomer with the composition comprising the material with the structure,



where the integers R<sub>1</sub> and R<sub>2</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> or hydrogens. Substituents R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> may also be nitro. They may be identical or different permutations of the above substituents.

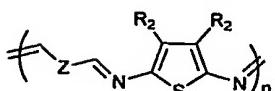
5. An electrically conducting oligomer with the composition comprising the material with the structure,



where the integers R<sub>4</sub> and R<sub>5</sub> may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> or hydrogens. Radical R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> may also be

$\text{NO}_2$ . They may be identical or different permutations of the above radicals. The radical Z may be a divalent aryl group comprising 6 carbons, heteroaryl comprising 4 carbons and a nitrogen or oxygen or selenium or tellurium, heteroaryl comprising 5 carbons and a nitrogen, stilbene, naphthalene, anthracene, acridine, fluorene, azobenene, biphenyl, diphenylsulfone, anthraquinone, diphenylmethane.

6. An electrically conducting oligomer with the composition comprising the material with the structure,



with the integers  $R_2$  may be aliphatic, aromatic, heteroatomic, hydrophilic, or hydrophobic. These groups may be aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains with C<sub>1</sub>-C<sub>12</sub> alkoxy groups, C<sub>6</sub>-C<sub>14</sub> aromatic systems, cyano, ester groups CO<sub>2</sub>Y with Y aliphatic C<sub>2</sub>-C<sub>12</sub>, aliphatic C<sub>2</sub>-C<sub>4</sub> aliphatic chains, -O(CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> or hydrogens. The radicals may be identical or different permutations of the above radicals. The radical Z may be a divalent aryl group comprising 6 carbons, heteroaryl comprising 4 carbons and a nitrogen or oxygen or selenium or tellurium, heteroaryl comprising 5 carbons and a nitrogen, stilbene, naphthalene, anthracene, acridine, fluorene, azobenzene, biphenyl, diphenylsulfone, anthraquinone, diphenylmethane.

7. The composition of claim 1 where the dopant is a p-type dopant.

8. The composition of claim 2 where the dopant is a p-type dopant.

9. The composition of claim 3 where the dopant is a p-type dopant.

- 10.** The composition of claim 4 where the dopant is a p-type dopant.
- 11.** The composition of claim 5 where the dopant is a p-type dopant.
- 12.** The composition of claim 6 where the dopant is a p-type dopant.
- 13.** The composition of claim 1 where the dopant is a n-type dopant.
- 14.** The composition of claim 2 where the dopant is a n-type dopant.
- 15.** The composition of claim 3 where the dopant is a n-type dopant.
- 16.** The composition of claim 4 where the dopant is a n-type dopant.
- 17.** The composition of claim 5 where the dopant is a n-type dopant.
- 18.** The composition of claim 6 where the dopant is a n-type dopant.
- 19.** The composition of claim 1 where the polymerization can be done with one stoichiometric equivalent of a monoaldehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.

- 20.** The composition of claim 2 where the polymerization can be done with two stoichiometric equivalents of a monoaldehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.
- 21.** The composition of claim 3 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.
- 22.** The composition of claim 4 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.
- 23.** The composition of claim 5 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.

- 24.** The composition of claim 6 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in alcoholic solvents such as but not limited to ethanol, methanol, isopropanol, butanol; benzene and/or toluene by azeotropic distillation; wet or anhydrous DMF; wet or anhydrous DMSO; wet or anhydrous THF; etc with temperatures from 25° to 120° C.
- 25.** The composition of claim 1 where the polymerization can be done with one stoichiometric equivalent of a monoaldehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.
- 26.** The composition of claim 2 where the polymerization can be done with two stoichiometric equivalents of a monoaldehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.
- 27.** The composition of claim 3 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.
- 28.** The composition of claim 4 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.

29. The composition of claim 5 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.
30. The composition of claim 6 where the polymerization can be done with one stoichiometric equivalent of a dialdehyde and diamine in the absent of solvent with temperatures from 50° to 120° C.
31. The composition of claim 1 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
32. The composition of claim 2 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
33. The composition of claim 3 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
34. The composition of claim 4 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium

sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.

35. The composition of claim 5 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
36. The composition of claim 6 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
37. The composition of claim 1 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.
38. The composition of claim 2 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.

- 39.** The composition of claim 3 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.
- 40.** The composition of claim 4 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.
- 41.** The composition of claim 5 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.
- 42.** The composition of claim 6 where the polymerization can be done with the use of acid catalysts between 5 – 10 mol % is not strictly required but may be in the form of organic or mineral acids including but not limited to trifluoroacetic acid, acetic acid, hydrochloric acid, sulphuric acid, etc. to accelerate oligomerization.
- 43.** The composition of claim 1 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.

- 44.** The composition of claim 2 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
- 45.** The composition of claim 3 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
- 46.** The composition of claim 4 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
- 47.** The composition of claim 5 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.
- 48.** The composition of claim 6 where the polymerization can be done with dehydrating reagents such as but not limited to anhydrous magnesium sulfate, anhydrous sodium

sulfate, activated molecular sieves, activated neutral or acidic aluminum oxide, anhydrous silica gel, etc can be used to shift the equilibrium in favour of the product.

49. The composition of claim 3 where the molecular weight can be controlled from 1000 to 100 000 by varying the concentration of the reagents in the solvent.
50. The composition of claim 4 where the molecular weight can be controlled from 1000 to 100 000 by varying the concentration of the reagents in the solvent.
51. The composition of claim 5 where the molecular weight can be controlled from 1000 to 100 000 by varying the concentration of the reagents in the solvent.
52. The composition of claim 6 where the molecular weight can be controlled from 1000 to 100 000 by varying the concentration of the reagents in the solvent.
53. The composition of claim 3 where the polymerization can be resumed with the composition from claims 3 to 4 by adding the compositions followed by increasing the concentration.
54. The composition of claim 4 where the polymerization can be resumed with the composition from claims 3 to 4 by adding the compositions followed by increasing the concentration.
55. The composition of claim 5 where the polymerization can be resumed with the composition from claims 3 to 4 by adding the compositions followed by increasing the concentration.

- 56.** The composition of claim 6 where the polymerization can be resumed with the composition from claims 3 to 4 by adding the compositions followed by increasing the concentration.
- 57.** The composition of claim 1 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 58.** The composition of claim 2 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 59.** The composition of claim 3 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 60.** The composition of claim 4 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 61.** The composition of claim 5 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 62.** The composition of claim 6 to be used for electronic materials, light emitting diodes, field effect transitions, device composition leading to electronic devices, etc.
- 63.** The composition of claim 1 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.
- 64.** The composition of claim 2 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.
- 65.** The composition of claim 3 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.
- 66.** The composition of claim 4 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.

- 67.** The composition of claim 5 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.
- 68.** The composition of claim 6 is a quaternary ammonium salt of an unreactive non-nucleophilic anion.
- 69.** The composition of claim 1 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 70.** The composition of claim 2 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 71.** The composition of claim 3 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 72.** The composition of claim 4 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 73.** The composition of claim 5 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 74.** The composition of claim 6 where the dopant is selected from the group consisting of chlorine, bromine, iodine, SbF<sub>5</sub>, AsF<sub>5</sub>, PF<sub>5</sub>, AgX, NO<sub>2</sub>X, and NOX where X is an unreactive, non-nucleophilic anion.
- 75.** The composition of claim 1 where the dopant is a Lewis acid selected from the group consisting of FeCl<sub>3</sub> or AlCl<sub>3</sub>.

76. The composition of claim 2 where the dopant is a Lewis acid selected from the group consisting of  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .
77. The composition of claim 3 where the dopant is a Lewis acid selected from the group consisting of  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .
78. The composition of claim 4 where the dopant is a Lewis acid selected from the group consisting of  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .
79. The composition of claim 5 where the dopant is a Lewis acid selected from the group consisting of  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .
80. The composition of claim 6 where the dopant is a Lewis acid selected from the group consisting of  $\text{FeCl}_3$  or  $\text{AlCl}_3$ .
81. A composition of claim 3 wherein n is 1 to 50 000.
82. A composition of claim 4 wherein n is 1 to 50 000.
83. A composition of claim 5 wherein n is 1 to 50 000.
84. A composition of claim 6 wherein n is 1 to 50 000.
85. Compositions of claim 1 wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.
86. Compositions of claim 2 wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.
87. Compositions of claim 3 wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.
88. Compositions of claim 4 wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.
89. Compositions of claim 5 wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.

- 90.** Compositions of claim **6** wherein a thin film can be obtained by casting from any volatile organic solvent by spin coating or solvent evaporation.
- 91.** The method of claim **82** wherein said substrate is glass or fused silica.
- 92.** The method of claim **83** wherein said substrate is glass or fused silica.
- 93.** The method of claim **84** wherein said substrate is glass or fused silica.
- 94.** The method of preparing an optical device comprising the steps of:
- (a) applying to an optically transparent substrate a solution in an organic solvent of an electron donor-acceptor complex of a conjugated aromatic polyazomethine compound comprised of the repeating units in claims **1** through **6** and
- (b) evaporating said solvent, producing a film of said complex on said substrate.
- 95.** The method of claim **85** wherein said film of said complex on said substrate provides a third-order nonlinear optical device.
- 96.** The method of claim **85** comprising an additional step (c) decomposing said complex on said substrate, producing a film of said polyazomethine compound on said substrate.
- 97.** The method of claim **87** wherein said film of said polyazomethine compound on said substrate provides a third-order nonlinear optical device.
- 98.** The composition from claim **1** to be used as a molecular wire.
- 99.** The composition from claim **2** to be used as a molecular wire.
- 100.** The composition from claim **3** to be used as a molecular wire.
- 101.** The composition from claim **4** to be used as a molecular wire.
- 102.** The composition from claim **5** to be used as a molecular wire.
- 103.** The composition from claim **6** to be used as a molecular wire.

- 104.** The composition from claim 1 to be used in a light emitting diode.
- 105.** The composition from claim 2 to be used in a light emitting diode.
- 106.** The composition from claim 3 to be used in a light emitting diode.
- 107.** The composition from claim 4 to be used in a light emitting diode.
- 108.** The composition from claim 5 to be used in a light emitting diode.
- 109.** The composition from claim 6 to be used in a light emitting diode.
- 110.** The composition from claim 3 obtained by applying a dialdehyde and a diamine separately onto a surface followed by heating to evaporate the water.
- 111.** The composition from claim 4 obtained by applying the difunctional group onto a surface followed by heating to evaporate the water.
- 112.** The composition from claim 5 obtained by applying a dialdehyde and a diamine separately onto a surface followed by heating to evaporate the water.
- 113.** The composition from claim 6 obtained by applying a dialdehyde and a diamine separately onto a surface followed by heating to evaporate the water.
- 114.**